

Polymers in linear shear flow: a numerical study

A. CELANI¹, A. PULIAFITO^{1,3} and K. TURITSYN^{1,2,3}

¹ *Institut Non Linéaire de Nice - UMR 6618 CNRS, 1361, Route des Lucioles, 06560 Valbonne, France*

² *Landau Institute for Theoretical Physics - Kosygina 2, Moscow 119334, Russia*

³ *CNLS, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

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Abstract. – We study the dynamics of a single polymer subject to thermal fluctuations in a linear shear flow. The polymer is modeled as a finitely extendable nonlinear elastic (FENE) dumbbell. Both orientation and elongation dynamics are investigated numerically as a function of the shear strength, by means of a new efficient integration algorithm. The results are in agreement with recent experiments.

Introduction. – Nowadays, thanks to the development of effective experimental techniques, it is possible to follow the motion of a single macromolecule in a flow, either laminar or turbulent [1–8, 11–18]. This is of crucial importance for applications in polymer processing [19] and biophysics [1]. Dynamical properties of biomolecules have been explored in detail (see e.g. [1–5, 11–14] for DNA and [15] for chromatin) and protein–macromolecule interactions have been studied [16–18].

The formulation of theoretical models (see e.g. [19]) able to reproduce qualitatively and quantitatively these measurements represents an important step towards the understanding of single-molecule biophysics. An extensive analysis of single polymer dynamics in simple flows has been conducted in a series of papers by Chu and coworkers, Larson and coworkers and Shaqfeh and coworkers (see [1–8] and references therein). Here we mention in particular two recent papers where the statistics of orientation and conformation of long-chain molecules in linear shear flows has been studied in great detail, with a direct comparison with numerical models [9, 10]. An intrinsic difficulty is represented by the large number of degrees of freedom required to describe the polymer conformation, and thus its dynamics. Nonetheless, non-trivial aspects of polymer–fluid interactions may be accounted for and even explained at a semi-quantitative level by means of simple, few degrees of freedom models. One of the simplest, yet reliable, model is the finitely extendable nonlinear elastic dumbbell (FENE) [19]. The polymer is described by its end-to-end distance vector \mathbf{R} and the microphysical properties are essentially dumped into two parameters: $1/\gamma$, the longest elastic relaxation time of the macromolecule, and ζ , its friction coefficient with the surrounding solvent. Nonlinear elastic

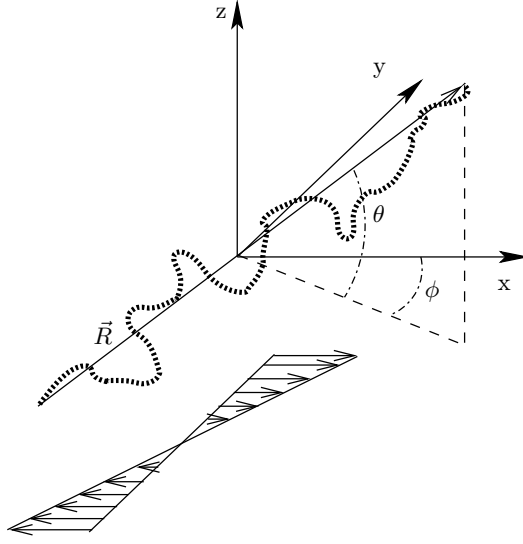


Fig. 1 – A sketch of the geometry of polymer motion in a linear shear flow.

effects must be accounted for whenever the polymer is considerably stretched, as is the case of shear flows [4]. The geometry of this problem is depicted in Fig. 1. The polymer spends a large fraction of time in elongated configurations along the shear direction. In the following we will present numerical results about end-to-end orientation, elongation and about the statistics of tumbling times. The latter is defined as the time spent between two successive “flips” of the polymer ends (see Fig. 2). Tumbling can occur via different pathways, e.g. passing by a coiled state or through folded configurations: those details cannot be addressed within the single-dumbbell model and will be the subject of future study.

From experiments to numerics. – Single polymer orientation and tumbling dynamics was recently studied experimentally by Steinberg *et al.* [12] with a 10^{-3} ppm solution of λ -DNA

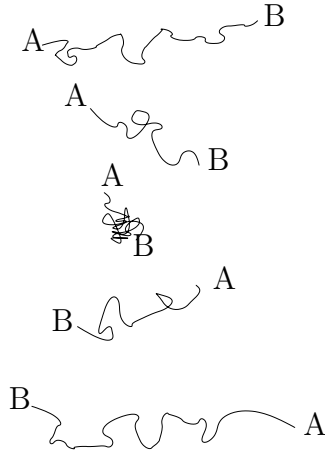


Fig. 2 – Four possible stages of a tumbling event.

molecules labeled with fluorescence methods (but see also the experiments presented in [9,10]). To resolve the angular dynamics two different flow configurations were used: one was generated by two discs one of which was rotating with uniform angular velocity Ω and the other flow was obtained by a boundary layer in a micro-channel produced with the soft lithography method (see [12] and references therein for details).

To reproduce the physical situation of [12] we studied a FENE dumbbell in a simple shear flow $\vec{v} = (sy, 0, 0)$, sensing thermal fluctuations (see Fig. 1). The equation describing the evolution of the end-to-end vector of the polymer is:

$$\dot{R}_i = s \delta_{ix} R_y - \frac{\gamma R_i}{2} (1 - R^2/R_m^2)^{-1} + \sqrt{\gamma R_0^2} \eta_i(t) \quad (1)$$

where $R_0 = K_B T/H$, $\gamma = 4H/\zeta$, $\boldsymbol{\eta}$ is a three-dimensional white noise with zero mean and correlation $\langle \eta_i(t) \eta_j(t') \rangle = \delta_{ij} \delta(t - t')$, R_m is the maximum length of the polymer, K_B is the Boltzmann constant, T is the temperature, ζ is the isotropic drag coefficient, and H the spring constant.

Even if the single-FENE-dumbbell model does not reproduce precisely the behavior of real molecules [8], we can set the parameters of our model, R_0 , R_m , γ , as close as possible to their corresponding experimental values [4,12]: we choose $R_0 \simeq 1 \mu\text{m}$, $R_m/R_0 \simeq 21$, $\gamma \simeq 0.01 \text{ s}^{-1} \div 1 \text{ s}^{-1}$.

The orientation dynamics has been investigated for rigid spheroid by Hinch and Leal [20]. As for polymers, at large Weissenberg numbers $Wi = s/\gamma$, where s is the shear rate, the basic ingredients of the polymer dynamics can be summarized as follows [7, 20–25]: due to the shear flow the polymer tends to reach the unstable equilibrium configuration where it is fully extended along the shear direction. In polar coordinates $(R, \theta, \phi) = (R_m, 0, 0 \text{ or } \pi)$. The effect of thermal noise is to drive the polymer away from this configuration. The most probable value of θ is zero, due to the symmetry of the dynamics along the z axis. However, large fluctuations in the off-shear-plane angle can occur. The most probable value for ϕ will be slightly larger than 0, or π : the symmetry-breaking effect of shear causes the polymers to “hesitate” for some time before crossing the x axis and then give rise to a tumbling event. Few results can be obtained analytically for this model, except for the linear case where $R_m/R_0 \rightarrow \infty$.

Numerical algorithm. – Several numerical methods have been proposed to simulate polymer dynamics (see for example [26]). A commonly encountered problem with nonlinear elastic models is the loss of accuracy close to the singularity $R \rightarrow R_m$. In order to overcome this problem it is possible to perform a change of variables in the vicinity of R_m that removes the singularity and allows to use a straightforward time-marching scheme. This method can be easily extended to other nonlinear models [27] as well as to other flows.

Eq. (1) can be solved by any stochastic discretization scheme (Euler-Itô in our case) in the region $R < R_{thr}$, where R_{thr} is a fraction of R_m , say $0.5 R_m$. Whenever R exceeds the threshold we switch to polar variables $(R, \hat{\mathbf{n}})$, where $\hat{\mathbf{n}}$ is the unity vector describing the orientation of the polymer $\hat{n}_i = R_i/R$, and then to the new variables $(z, \hat{\mathbf{n}})$, where

$$z = -\frac{R_m}{2} \left(1 - \frac{R}{R_m}\right)^2. \quad (2)$$

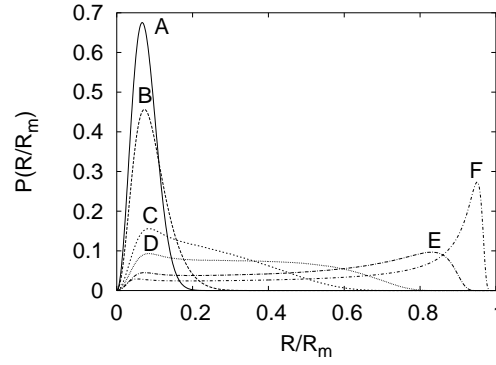


Fig. 3 – The PDF of elongation plotted for $Wi = 0, 1, 5, 10, 40, 200$ (from A to F).

This relation can be easily inverted to give R as a function of z . After computing all the contact terms in the Itô convention we have the following equations for $(z, \hat{\mathbf{n}})$:

$$\dot{z} = -\gamma R \left(1 + \frac{R}{R_m}\right)^{-1} + s \hat{n}_x \hat{n}_y R \left(1 - \frac{R}{R_m}\right) + \frac{\gamma R_0^2}{2} \left(\frac{2}{R} - \frac{1}{R_m}\right) + \sqrt{\gamma R_0^2} \left(1 - \frac{R}{R_m}\right) \hat{n}_i \eta_i(t) \quad (3)$$

$$\partial_t \hat{n}_i = s(\hat{n}_y - \hat{n}_y \hat{n}_x^2) \delta_{ix} - \frac{\gamma R_0^2}{R^2} \left(1 - \frac{R}{R_m}\right)^2 \hat{n}_i + \frac{\sqrt{\gamma R_0^2}}{R} (\eta_i(t) - \eta_j(t) \hat{n}_j \hat{n}_i). \quad (4)$$

which is regular in the neighborhood of $R = R_m$, i.e. $z = 0$.

Results. – The Probability Density Function (PDF) of the modulus of the conformation vector depends strongly on Wi . At sufficiently small $Wi \approx 1$ the statistics does not differ much from the linear elastic case, since $R \ll R_m$. The PDF in the FENE case can be computed analytically only in asymptotic regimes [25, 28]. The numerical result is shown in Fig. 3 for several Weissenberg numbers. At very large Wi the elongation PDF presents a peak with height scaling as $Wi^{2/3}$ and width as $Wi^{-2/3}$ (not shown). This result is in agreement with the predictions of Ref. [23]. As a side remark we notice that experimental measurements of the elongation PDF at Wi as large as $Wi = 76$ do not display a peak near R_m (see [8] and fig. 5 of [4]) as well as numerical results of multi-beads models (see figs. 4, 5 in [8] and the discussion therein).

The orientation of polymers follows the qualitative picture drawn in the linear elastic case [24, 25], even though there appear important quantitative differences. The PDF of the in-shear-plane angle ϕ is shown in Fig. 4. The probability is concentrated in the vicinity of $\phi = 0, \pi$ with a peak width at half height ϕ_t , whose dependency on Wi is shown in Fig. 5. The case of a linear elastic dumbbell $R_m = \infty$ is shown for comparison. The angle ϕ_t decreases with Wi in both cases, i.e. the larger is Wi the narrower is the region around the x axis where the polymer spends most of its time. The scaling can be derived by simple physical arguments: following Chertkov *et al.* [22] the evolution equation for ϕ in the region $\phi \ll 1$ is approximated by $\partial_t \phi = -s\phi^2 + \sqrt{\gamma R_0^2/R^2} \eta_\phi$, where η_ϕ is a white noise. Thus ϕ_t can be estimated balancing shear and noise terms in the right hand side terms, i.e. $\phi_t \sim Wi^{-1/3} (R_0/R)^{2/3}$. At large Wi , for a linear elastic dumbbell one has $R \propto Wi$, yielding $\phi_t \sim Wi^{-1}$, whereas for a nonlinear elastic force one estimates $R \sim R_m$ to find $\phi_t \sim Wi^{-1/3}$. The tails of the PDF follow closely the distribution $\sin^{-2} \phi$ dictated by the shear (see Fig. 4).

The agreement with the experiments is very good [12]: the scaling in the tail follows $\sin^{-2} \phi$,

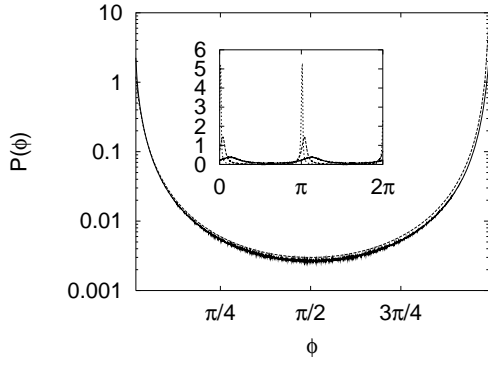


Fig. 4

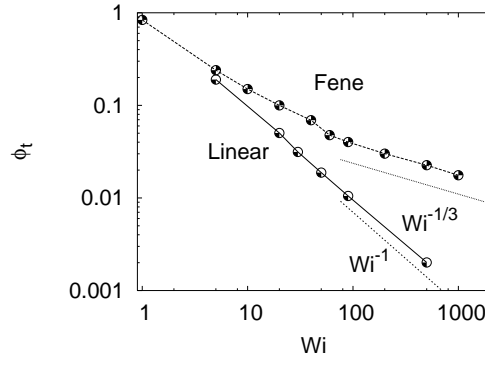


Fig. 5

Fig. 4 – The PDF of the angle ϕ plotted with $\sin^{-2}\phi$. In the inset the PDF in linear scale plotted for $Wi = 1, 5, 40$.

Fig. 5 – The behavior of ϕ_t as a function of Wi .

and the dependence of ϕ_t on Wi is close to the theoretical prediction already for $Wi = 25$.

The marginal PDF of the angle θ is presented in Fig. 6. The tails decay as θ^{-2} , with a scaling range increasing with Wi . The algebraic behavior has been observed in [12] for $Wi = 17.6$, and even if Wi is not very high the agreement is remarkable. The probability density of θ for small angles $\phi \sim \phi_t$, or equivalently the joint PDF $P(\theta, \phi = 0)$, shows a neat power law close to θ^{-3} for $\theta \gg \theta_t$. This nontrivial scaling behaviour has been predicted theoretically and observed numerically for the linear elastic case in Refs. [22, 24, 25]. The width of the peak of the $P(\theta)$ at half height, θ_t , decays as $Wi^{-1/3}$ for the nonlinear elastic case. The agreement with experimental data is perfect [12].

Note that the cross-over between the linear elastic case $\phi_t \sim \theta_t \sim Wi^{-1}$ and the FENE case $\phi_t \sim \theta_t \sim Wi^{-1/3}$ occur at $Wi \sim 1$, as measured experimentally.

For what concerns the tumbling times statistics there are two possible definitions [25]: (i) given an appropriate threshold value in R that defines the coiled state for the polymer, one can compute the time spent during two successive coiled states [12]. (ii) one can consider the time between two subsequent crossings of the plane $\phi = \pi/2$.

Both definitions are ambiguous for small values of Wi , i.e. when the polymer spends most of its time in a coiled state. For large tumbling times the PDF is exponential for both definitions of τ , $P(\tau) \sim \exp[-E\tau]$ (see Fig. 8). This is a robust feature of this phenomenon [12, 22]. Experimental measurements of the tumbling time are possible only following the first definition, due to lack of angular resolution [12].

The exponent E of the tail in the linear elastic case is inversely proportional to the relaxation time of the polymer γ^{-1} . In the FENE case there is a non trivial dependence on Wi , as shown in Fig. 9. The scaling of the typical tumbling time $\tau_t \sim E^{-1}$ can be estimated at large Wi as follows: the angular motion in the region $\phi \sim \phi_t$ is driven by the thermal noise and is therefore diffusive. The diffusion coefficient is $D = \gamma(R_0/R)^2$ and therefore $\tau_t \sim \phi_t^2/D$. Substituting $R \propto R_0 Wi$ for the linear spring model and $R \sim R_m$ for the FENE model one obtains for E/γ the scalings Wi^0 and $Wi^{2/3}$, respectively.

The behavior of the PDF at $\tau \ll \tau_t$ is model dependent and should not be considered as

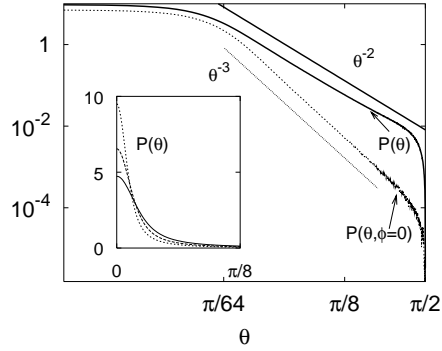


Fig. 6

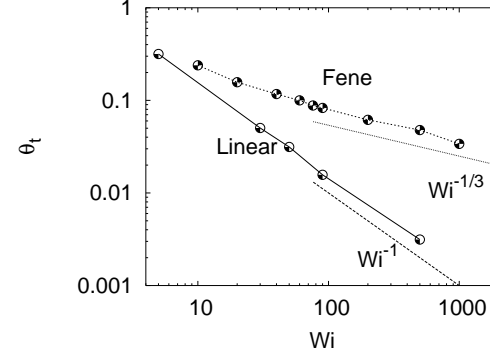


Fig. 7

Fig. 6 – The PDF of the angle θ plotted against θ^{-2} . In the inset the PDF in linear scale for $Wi = 20, 40, 100$.

Fig. 7 – The behavior of θ_t as a function of Wi .

relevant (see e.g. [25]). In experiments [12] the exponential tail of the PDF is observed and the dependence of τ_t on Wi is in accordance with theoretical arguments and numerical results.

Conclusions. – We studied the dynamics of a single FENE polymer immersed in a simple shear flow with thermal noise. The statistics of orientation, elongation and tumbling of the polymer have been analyzed in comparison with experimental measurements [12], previous numerical simulations [8, 25], and theoretical expectations [22–24]. Even if the large variety of conformations of real polymer can not be explored within such a simple model, single-FENE-dumbbell can reproduce semiquantitatively several aspects of the behavior of real polymers.

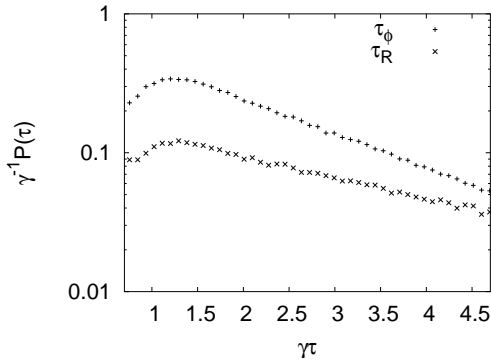


Fig. 8

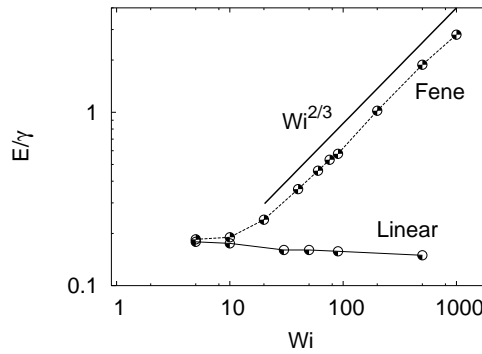


Fig. 9

Fig. 8 – The PDF of tumbling times: τ_R is the time elapsed between two nonadjacent coiled states, defined as the states where R is smaller than λR_0 ($\lambda = 1.5$ in this figure); τ_ϕ is defined as the time between two rotations of π in the angle ϕ . Here, $Wi = 76$.

Fig. 9 – The exponent E rescaled with the relaxation time as a function of Wi in the linear case and in the FENE case.

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